

98-334057/30

A60 E19 L03

FARH 96.12.11

HOECHST AG

DE 19651439-A1

96.12.11 96DE-1051439 (98.06.18) C07C 47/546, 17/16, 22/04, 255/33, 331/04, C08G 61/00, C09K 11/06, C07F 9/28, C07C 265/08, 47/55, 45/29

Preparation of biaryl derivative - by reacting two aryl derivatives to give intermediate product and reducing, selectively oxidising or exchanging with (pseudo)halogen

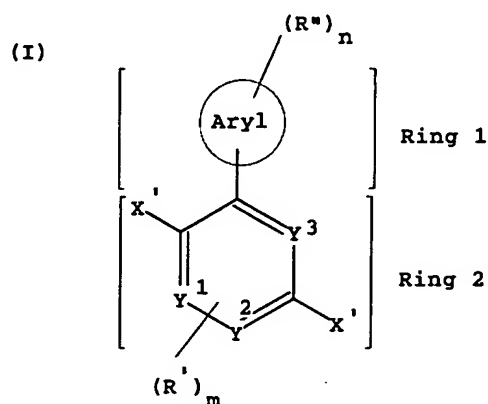
C98-103594

Addnl. Data: SPREITZER H, KREUDER W, BECKER H, KRAUSE J

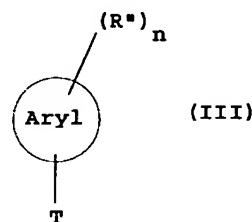
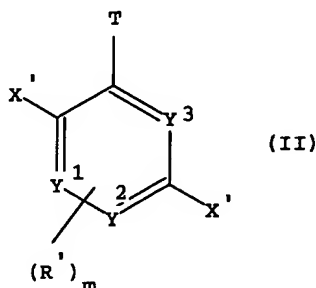
Preparation of biaryl derivative of formula (I) comprises: (A) reacting two aryl derivatives of formulae (II) and (III) in solvent in the presence of a palladium catalyst at 0-20°C to give an intermediate product of formula (IV); (B) if $X' = \text{COOR}^8$ (IVa), reducing to give $X = \text{CH}_2\text{OH}$ (IVb);

(Ca) selectively oxidising to give $X = \text{CHO}$ or (Cb) exchanging the OH group to a (pseudo)halogen to give $Z = \text{Cl, Br, I, CN, SCN}$ or NCO; and optionally (D) giving (I) with $Z = \text{Cl, Br, I, CN}$ or SCN by reacting with (I)

A(1-A2, 1-E, 1-E2, 1-E6, 1-E10) E(7-D, 10-A14A, 10-A15A, 10-A15E, 10-B1B, 10-D1C, 10-E4, 10-J2B3) L(3-D1, 3-H4A)

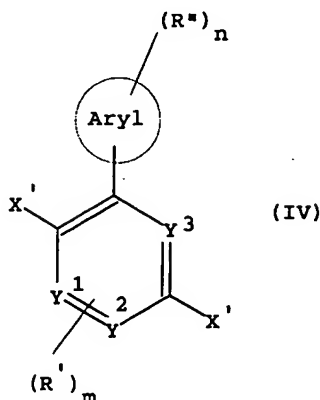


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DE 19651439-A+/I

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$Z = \text{PO}(\text{OR}^1)_2, \text{PO}(\text{R}^2)_2$ or $\text{P}(\text{R}^3)_3^+ \text{A}^-$;
 $X = \text{CH}_2\text{Z}$ or CHO ;

$Y^1 - Y^3 = \text{CH}$ or N ;
 $Z = \text{Cl, Br, I, CN, SCN, NCO, PO}(\text{OR}^1)_2, \text{PO}(\text{R}^2)_2$ or $\text{P}(\text{R}^3)_3^+ \text{A}^-$;
Aryl = 4-14C aryl;
 $\text{R}^1, \text{R}^2 = 1-20\text{C}$ alkyl or alkoxy where CH_2 group(s) can be substituted by O, S, CO, COO, OCO, NR^4 , $(\text{NR}^5\text{R}^{6+})^+ \text{OR}$ CONR^7 , H atom(s) can be substituted by F, CN, F, CL or 4-14C aryl optionally substituted by R^1 ;
 $\text{R}^1 - \text{R}^3 = 1-20\text{C}$ hydrocarbon;
 $\text{R}^4 - \text{R}^7 = \text{H}$ or 1-20C hydrocarbon;
 $\text{A}^- = \text{anion}$ or equivalent;
 $m = 0-2$;
 $n = 1-5$;
 $X' = \text{CH}_2\text{OH}$ or COOR^8 ;
one of T and $\text{T}' = \text{Cl, Br}$ or I or 1-12C perfluoroalkyl sulphonyl;
the other one of T and $\text{T}' = \text{SnR}_3$ or BQ_1Q_2 ; $\text{Q}_1, \text{Q}_2 = \text{OH, 1-4C alkyl}$ or alkoxy, phenyl optionally substituted by halogen or 1-4C alkyl or alkoxy, or halogen, or $\text{Q}_1 + \text{Q}_2 = 1-4\text{C alkylene dioxy}$ optionally substituted by 1-4C alkyl; and
 $\text{R}^8 = \text{H}$ or 1-12C hydrocarbon.

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Also claimed are the above biaryl derivatives per se.

MORE SPECIFICALLY

$Z = \text{Cl, Br, CN, PO(OR}^1\text{)}_2, \text{PO(R}^2\text{)}_2 \text{ or P(R}^3\text{)}_3^+ \text{A}^-$; $\text{Y}^1 - \text{Y}^3 = \text{CH}$, Aryl = phenyl, 1- or 2-naphthyl, 1-, 2- or 9-anthracenyl, 2-, 3- or 4-pyridinyl, 2-, 4- or 5-pyrimidinyl, 2-pyrazinyl, 3- or 4-pyridazinyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinoline, 2- or 3-thiophenyl, 2- or 3-pyrrolyl, 2- or 3-furanyl or 2-(13,4-oxadiazol)yl, $\text{R}^1 = 1\text{-12C alkoxy}$, $\text{R}^{2'} = 1\text{-12C alkyl or alkoxy}$, $m = 0 \text{ or } 1$ and $n = 1\text{-}3$.

USE

The biaryl derivatives are used in the preparation of polymers (claimed) which are useful as electroluminescence materials.

ADVANTAGE

Gives high purity.

PREFERRED PREPARATION

$\text{T} = \text{I, Br, Cl or 1-12C perfluoroalkyl sulphonate}$ and $\text{T}' = \text{QR}_1\text{R}_2$; $\text{X} = \text{COOR}^8$.

In step (B), the intermediate product (IV) is obtained by reaction with (i) LiAlH_4 , diisobutyl aluminium hydride, THF or toluene; (ii)

borohydrides; (iii) H in the presence of a catalyst; or (iv) Na or NaH.

In step (Ca), product (IVa) is obtained by oxidation with DMSO/oxalylchloride or either pyridinium chlorochromate or pyridinium chromate.

In step (Cb), product (IVb) is obtained by reacting with HCl or HBr or either thionyl chloride or thionyl bromide in a compound of formula (Ib) (I: $\text{X} = \text{Cl or Br}$).

In step (D), a compound of formula (Ib) is obtained by reaction with a trialkyl phosphate in a bisphosphate or formula (Ic) (I: $\text{X} = \text{PO(R}^1\text{)}_2$).

EXAMPLE

30.1 g 2-bromoterephthalic acid diethyl ester, 27.6 g K_2CO_3 , 140 ml toluene, 26.7 g 4-hexyloxyphenyl boronic acid and 1.16 g $\text{Pd(PPh}_3\text{)}_4$ were reacted at 85°C under Ar, followed by work-up to give 44.7 g 2-(4'-hexyloxyphenyl) terephthalic acid diethyl ester as a yellow-brown oil of purity 85%.

40 g of the product was treated with 5.3 g LiAlH_4 in 200 ml THF, followed by work-up to give 20.3 g 2,5-bishydroxymethyl-4'-hexyloxybiphenyl as colourless needles of purity above 98% and m.pt. $72.5\text{-}74^\circ\text{C}$.

200 mmol HBr in HAc was mixed with 12.6 g of the product. Work-up

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gave 16.9 g 2,5-bisbromomethyl-4'-hexyloxybiphenyl as a clear, honey coloured oil of purity above 98%.
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